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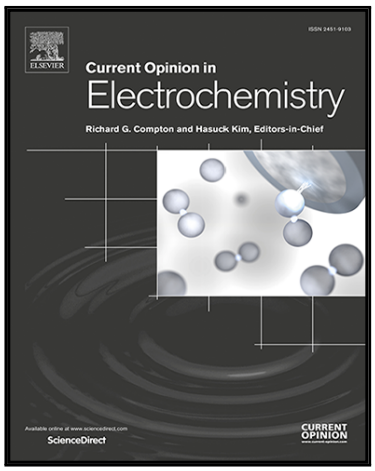

Heterogeneous electrocatalysis of formic acid oxidation on platinum single crystal electrodes

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Highlights

- Electrocatalysis of formic acid oxidation on platinum single crystal electrodes modified by adatoms is reviewed
- The different behavior of the adatoms is described
- Models describing the observed effect of the adatoms are presented.
- A mechanism for the electrocatalysis is presented combining experiments and theoretical results.

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Heterogeneous electrocatalysis of formic acid oxidation on platinum single crystal electrodes.

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Abstract

The oxidation of formic acid on single crystal platinum electrodes modified by a constant coverage of irreversibly adsorbed adatoms is described in this review. This subject has been studied for a wide period and the available information is huge. In consequence, we have selected the self-consistent set of results, which try to explain the nature of the electrocatalytic behaviour of the adatoms and to point out the research details that should be addressed in the future. All the results have been linked to the increasing understanding of formic acid oxidation on single crystal platinum electrodes in absence of foreign adatoms.

Introduction

Formic acid oxidation (FAO) reaction on platinum electrodes is a model reaction, which can be used to check our understanding in the oxidation of possible organic fuels. Despite the fact that formic acid itself can be considered as a suitable fuel, it is clear that there are other molecules that could be more appropriate fro using them in a fuel cell. However, their oxidation process is much more complex. This complexity arises from its oxidation kinetics and it is believed that if we can understand the kinetics of these processes and identify the rate determining steps and, we would be able to find better electrocatalysts. In this respect, the simplest molecule that can be used as the reasonably starting point is formic acid and FAO has been widely studied in the past and still new data is being published, clarifying

some issues in the mechanism. In this report, we will attempt to select relevant papers that generated the actual state of knowledge, as far as we understand.

FAO kinetics is the paradigm of the so-called dual path mechanism [1], widely present in other organic fuel reactions: the reaction splits in two parallel sets of elementary steps, one leading to the desired final product CO_2, at relatively low potentials and running through the so-called active intermediate, and a parallel chemical dehydration step leading to adsorbed CO, which will be further oxidized to CO_2 at higher potentials.

$$\mathrm{HCOOH} \begin{cases} \nearrow\ \mathrm{Active\ \ Intermediate} \xrightarrow{E_1} \mathrm{CO_2 + 2H^+ + 2e} \\ \searrow\ \mathrm{CO + H_2O} \xrightarrow{E_2} \mathrm{CO_2 + 2H^+ + 2e} \end{cases} \qquad E_2 > E_1$$

It is well known that FAO is a structure-sensitive process which depends on the surface orientation of the platinum electrocatalyst, this fact being demonstrated for both reaction paths [2-5]. Adsorbed CO, the poisoning intermediate, inhibits the overall reaction process. For this reason, the inhibition of this poisoning path would lead to the enhancement of the FAO rate and has been the subject of many efforts. Incidentally, it was observed that the adsorption of some foreign adatoms enhanced the electrochemical reaction rate. The most relevant papers, in which fundamental interpretation of data is attempted, can be found in the works by S. Motoo, who classified the effect of surface adatoms on polycrystalline platinum into three groups: i) those inducing electronic effects to the surface of the material, ii) those acting as a third body, simply inhibiting the dehydration reaction and iii) those playing a bifunctional role, in such a way that they would easily adsorb oxygen suitable to oxidize adsorbed CO at lower potentials than on pure platinum [6,7].

It was thus logical to study the role of the different adatoms on single crystal platinum substrates to get insight in surface reactivity. The ideal situation for the catalysis is that in which the surface composition could be kept constant in a wide potential range. This excluded

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experiments in which metals were deposited in underpotential deposition (UPD) conditions, because, in these latter cases, the composition of the surface depends on the applied potential. Thus, the so-called irreversibly adsorbed adatoms [8,9], many of them having catalytic effects at polycrystalline platinum, are the best candidates to be analyzed at well-defined platinum single crystal surfaces, correlating coverage values and currents.

Experimental details.

Fundamental studies require a careful control of the surface structure and cleanliness. Single crystal electrodes were prepared from single crystal beads by using usual procedures. They were flame annealed and cooled in convenient atmospheres. Voltammetry was used to check surface order of the surfaces and cleanliness of the cells. Irreversible adsorption was carried out either spontaneously at open circuit or at controlled potentials. To compare, adatom coverages are referred to the blockage of the platinum surface:

$$\theta_x = 1 - \theta_H = \frac{q_H^0 - q_H^x}{q_H^0}$$

where q_H^0 and q_H^x are the hydrogen adsorption charges for bare and adatom modified Pt electrode. The coverage defined in this way (θ_x) is a relative coverage, in which the value 1 is assigned for a layer in which all the Pt sites have been blocked by the adatom, i.e., no hydrogen adsorption is observed. In some cases, it is possible to calculate a absolute coverage values (Θ_x), defined as the number of adatoms by Pt surface atom, using some redox process undergone by the surface adatom [10]. Poison formation ability was performed at open circuit. In all cases, the CO coverage was estimated from its overall stripping charge without further correction.

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Surface structure of the adatom-covered single crystal platinum electrodes.

For electrocatalytic purposes, relative coverage values calculated from the decrease of the platinum adsorption ability can be used in the analysis of the data, but it seemed interesting to investigate the structure of the adlayers and the stoichiometry of the surface reactions undergone by the irreversibly adsorbed adatoms. These reactions usually involve the formation of an oxidized product at high potentials. This information could be further relevant in the study of other oxidation processes. The first information was taken from charge balancing between the increasing adatom related signal and the decrease of the substrate related one. This balance lead to linear plots in most cases and from them a general surface stoichiometry for the adatom redox process could be proposed under some hypothesis. These stoichiometry values are used to calculate absolute coverage values

Among the cases investigated, the As-Pt(111) system is likely the one that gave the best agreement between expected electrochemical reaction for the adatom and the surface blockage [11,12]. Other cases, particularly that of Bi-Pt(111) were less straight forward [13], because the surface stoichiometry for the surface reaction of bismuth gave an oxidized state with a +2 valency and adlayer reorganization was detected as the coverage reaches a given value. To try to explain this anomalous value, it was proposed that the species adsorbing oxygen in the redox process was the neighboring Pt sites and not the Bi adatoms [14,15]. This explanation is strange because Bi is a more electropositive adatom than As, for wich the adsorption of oxygen on the As adatoms was corroborated [12]. Therefore, there are still many details on surface reactivity that should be investigated to have clear picture of the structure of these electrocatalysts. It should be noted that these systems can be used in combination with other species, such as CO [16] and NO [17]

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Electrocatalysis on the Pt(111) substrate.

In general, the presence of irreversibly adsorbed adatoms on Pt(111) substrates lead to an increase of the current density at around 0.5 V, e.g. the potential at which the substrates show their maximal activity [18-25]. In the case study of Bi-Pt(111) electrodes, the activity increases linearly with the adatom coverage until a maximum was reached, then decreased when the adlayer was close to completion [18] (figure 1). For the different adatoms studied on the Pt(111), it was observed that the current densities were generally higher than those corresponding to the intrinsic activity of the Pt(111) substrates free of poison [19]. This behavior suggests that reaction requires free platinum sites, and that the enhancement takes place on those free sites close neighborhood to sites occupied by the adatom. It was also realized that the enhancement of the activity was dependent on the electronegativity of the adatom: better results were obtained with the less electronegative adatoms [21,26]. Additionally, temperature dependent studies revealed that the activation energy for the reaction diminished as the coverage increases [26,27]. Moreover, the values were around 20 kJ mol^{-1} for the Bi coverage that displays the higher activity.

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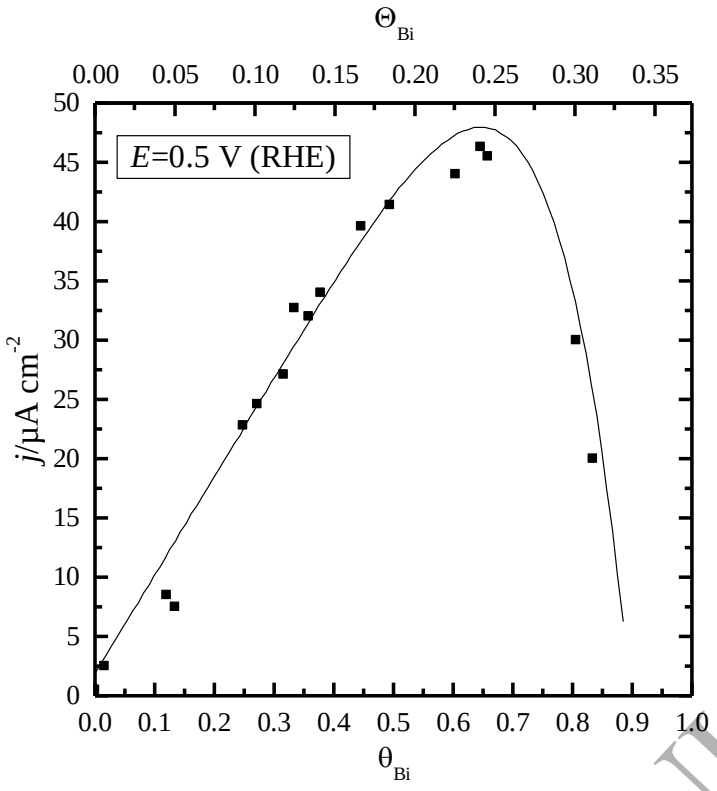

Figure 1. Current density for formic acid oxidation vs. bismuth coverage. The current has been measured at 0.5 V vs. RHE in 1 M $HClO_4$+ 0.5 M HCOOH for the Pt(111) [28]. The solid line represents the curve obtained according to the model of Ref [29]

On the other hand, when the poison path was studied, a drastic diminution in the amount of poisoning was observed for very low adatom coverages [30]. It should be stressed that the rate for CO formation on the Pt(111) electrode was significantly lower than that measured for other single crystal surfaces [31], but CO could be detected. Studies with stepped surfaces showed that CO was generated at the step sites and, once these sites were blocked by electropositive adatoms, poison was not generated at terraces [32-34]. Thus, it was also proposed that CO was formed on the defects of real Pt(111) electrodes. This characteristic behaviour of the adatoms does not fit with the expected for a third-body mechanism, especially because the high activity and the negligible poisoning at very low adatom coverage.

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Electrocatalysis on the Pt(100) substrate.

The unmodified Pt(100) surface has much higher activity than the Pt(111) electrode for both the direct reaction route and the poison formation [31,35]. When these surfaces are modified by adatoms, the most characteristic behavior is that of the Sb-Pt(100) system [36], whose response can be explained by a third body mechanism. In this case, poisoning decreases almost linearly with adatom coverage and its formation is completely inhibited before achieving full substrate blockage. When coverages reach those in which poisoning is negligible, the FAO current steadily increases and reaches a maximum value which is similar to the intrinsic activity of the substrate in absence of poison (figure 2). The diminution of the electrocatalytic activity at higher adatom coverage still suggests that the active sites are those of adatom uncovered platinum, but the absence of the poisoning for the coverage of maximum activity reveals that both reaction path have different site requirements [37,38]. Most of the studied adatoms follow qualitatively this behavior, but changing the maximum activity measured when the poison is completely inhibited. [36,37,39-42]

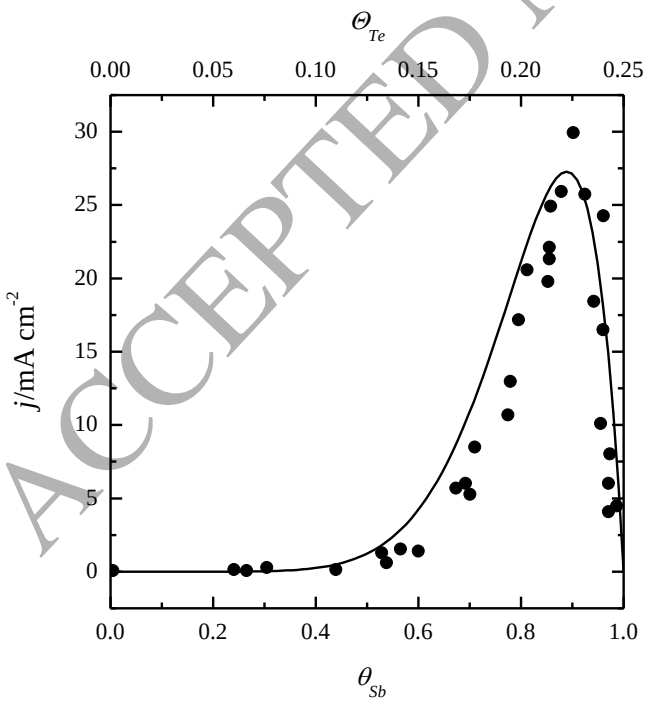

Figure 2. Current density for formic acid oxidation vs. antimony coverage. The current has been measured at 0.5 V vs. RHE in 0.5 M H_2SO_4+ 0.25 M HCOOH for the Pt(100) [28,36]. The solid line represents the curve obtained according to the model of Ref [29]

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Electrocatalysis on the Pt(110) substrate.

Unlike the preceding cases, the behavior of the adatoms at Pt(110) was only recently addressed, because it was difficult to analyze adatom adsorption at the Pt(110) substrates. Once solved in a reasonably way, FAO showed a different reactivity than the other two basal planes: as the adatom coverage increases, gains in activity are observed. This means that the reaction could take place at the adatom covered surfaces. A third-body inhibition of self-poisoning is found [43,44].

Electrocatalysis on the Pt nanoparticle substrates.

From the previous results using well-defined model electrodes, it seems clear that there is a great variety of responses when adatom-modified Pt electrodes are considered. In fact, it can be predicted that electrocatalysis will be always observed when adatom modified Pt nanoparticles are used. This is always the case, the differences being only due to small changes in the surface properties of the nanoparticles. It can be anticipated that the main problem for using these modified nanoparticles as electro catalysts deals with their stability, because the monolayer amount of the adatoms would likely dissolve with time. Only in cases in which it is possible to prepare intermetallic materials or when noble metals are used as modifiers, a reasonable stability could be expected. In the case of intermetallic compounds, they have shown an excellent activity [45-47]

Understanding the effect of the adatoms: statistic modelling and DFT studies.

From the observed behavior of the different adatoms on the studied single crystal electrodes, it was soon realized that the adatoms could have two different roles: they could take an active part in the activation of the direct reaction and/or they could act as inhibitors for the CO formation (third body effect). In order to distinguish both roles and to determine which role(s) was(were) following each adatom on the different surfaces, a statistic model was

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build [29]. In this model, the adatom was randomly distributed on the surface for a given coverage. For the case where the adatom has an active role in the reaction, it was proposed that the active site is the ensemble of a free site neighboring an adatom. Thus, the activity of those surfaces should be proportional to the number of those ensembles present on the surface for a given coverage. On the other hand, for the third body effect, it was proposed that CO formation requires two neighboring Pt sites whereas only one Pt site is involved in the direct route, in agreement with the experimental observed differences in the mechanism of both paths [41,48]. For low adatom coverages the activity is very low because the surface is readily covered by the poison. When the results from the two models were compared to the experimental results, it was found that the agreement was very good and they were able to explain the observed activity. It should be stressed that this model assumes that the adatom is adsorbed randomly on the surface, that is, there are no lateral interaction between the adsorbed adatoms and the adsorption of the adatom takes place in a specific site of the surface. In spite of these simplistic assumptions (lateral interactions and structural changes have been detected by STM [13]), the model gave a very good fitting allowing to establish the basic mechanisms for the catalysis. On one hand, for the Bi-Pt(111) surfaces, the model confirmed that the active role of Bi on the catalysis of the reaction (figure 1, solid line). For the other paradigmatic case, the Sb-Pt(100) system, the increase in activity observed for very high adatom coverages was related to the inhibition of poison formation on the isolated Pt sites, without discarding the enhancing effect of the Sb-Pt ensemble (figure 2, solid line).

To understand how the adatom on the Pt(111) electrode could activate the direct oxidation of formic acid, DFT calculations were carried out [26,27]. It was found that the Bi adatom on the Pt(111) surface had a partial positive charge, whereas the balancing negative charge was distributed over the Pt atoms. The positive charge of the Bi adatom facilitated the adsorption of formate from solution so that this species was bonded to the adatom by an oxygen (figure 3). In this configuration, the adsorbed formate can freely rotate using O-C axis.

In this rotation process, when the C-H bond in the formate species is pointing to the Pt surface, the cleavage of the C-H bond takes place giving rise to CO_2 and adsorbed hydrogen [26,49,50]. Owing to the potentials at which the reaction takes place, adsorbed hydrogen is oxidatively desorbed to the solution as a hydronium cation. These results validate the statistical model in which the active site is the Bi-Pt ensemble, and also explains the low activation barrier found experimentally and its diminution with the adatom coverage. The calculated activation barrier in the cleavage of the C-H bond for the Bi-adsorbed formate is almost negligible. These calculations imply that the system is acting as a bifunctional catalyst: the Bi adatom facilitates the adsorption of formate on the surface in the right configuration so that the neighboring Pt atom activates the cleavage of the C-H bond.

Figure 3. HCOO fragment adsorbed on the Bi-Pt(111) surface prior to the cleavage of the C-H bond. Adapted from [27]

Additionally, the DFT calculations also explained the experimentally observed increase in the activity of the Pt(111)-adatom system for the formic acid oxidation reaction as the adatom electronegativity of the adatom decreases [26]. When different adatoms were employed in the DFT calculations, it was observed that adsorption energy of formate was proportional to the partial positive charge retained by the adatom and this partial positive charge was, in turn, proportional to the electronegativity difference between Pt and the adatom. Thus, it can be inferred that the higher the difference in the electronegativity between Pt and the adatom is, the larger the positive charge is retained by the adatom, and the easier the adsorption of formate is obtained.

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DFT calcultions for the effect of Sb in the reaction are presented and a catalytic mechanism is proposed.

ACCEPTED MANUSCRIPT